

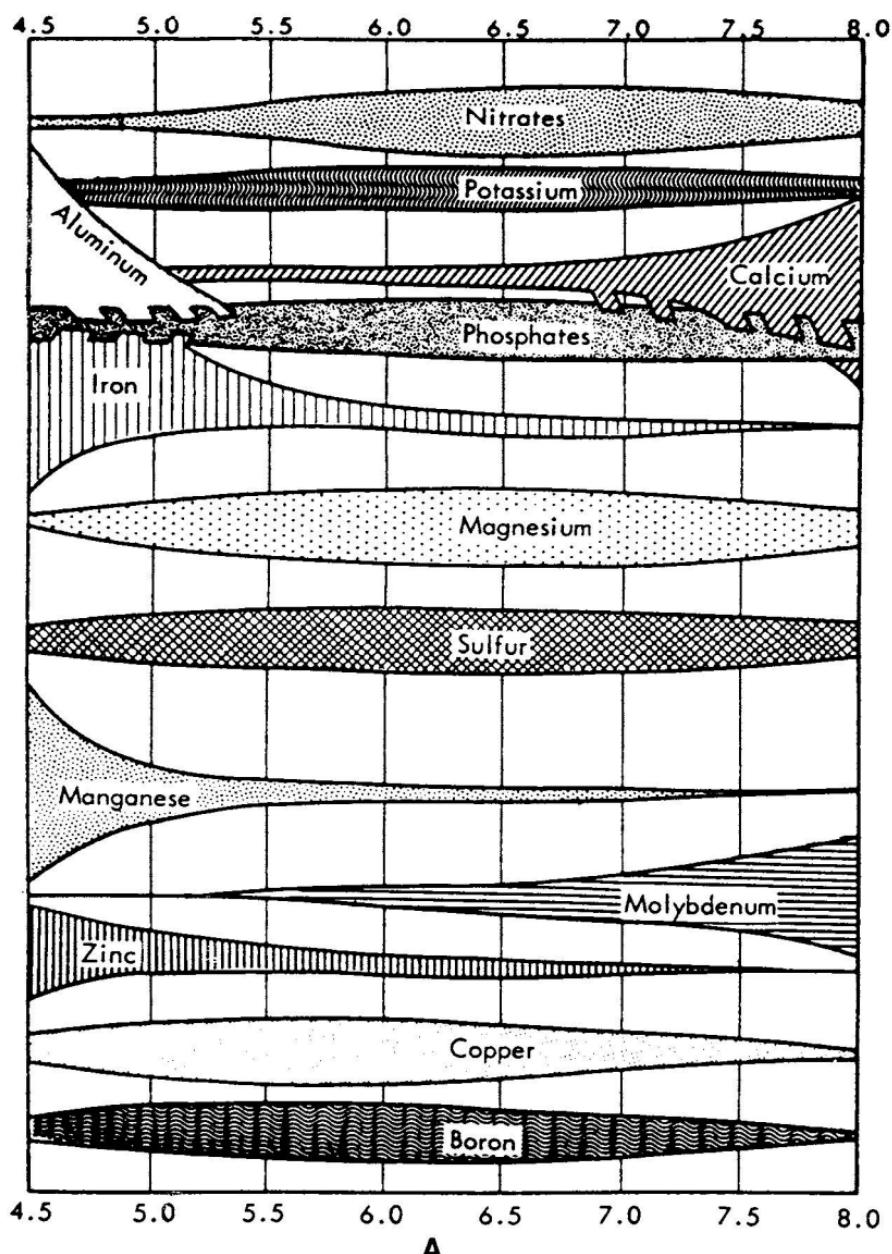
Soil acidity controls the solubility and precipitation of chemical compounds of all essential plant nutrients and is therefore a deciding factor on their availability. Soil acidity has a far-reaching influence on soil fertility and plant growth. For example, in strongly acidic soils Ca, Mg, P, B, and Mo become deficient, while Mn and Fe may reach toxic limits (Figure 6.1). Similarly, the availability of Cu, Fe, Zn, and Mn is reduced in alkaline calcareous soils. In mineral soils the pH (discussed later in this chapter) for the greatest availability of the most nutrients is 6.5 (Figure 6.1A), while in organic soils (peats and mucks) the optimum pH is about 5.5 (Figure 6.1B). In addition, in strongly acidic soils ( $\text{pH} < 5$ ) Al-toxicity poses a serious problem (Foy, 1992). An understanding of the nature of soil acidity and its management therefore forms an integral part of soil fertility.

## 6.1. ACIDS

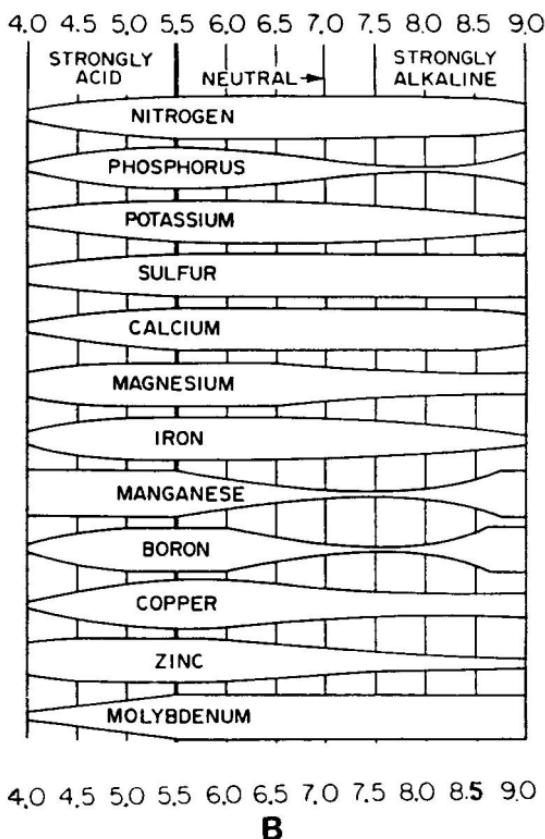
Although more precise definitions of acids and bases are available, the one that defines acids as substances yielding hydrogen ions (protons) when dissolved in water is the most practical and useful. Acids do differ in their rate of release of  $\text{H}^+$  ions (dissociation constant). Those that release  $\text{H}^+$  ions readily are known as strong acids. Examples are hydrochloric, sulfuric, and nitric acids. Acids that release their  $\text{H}^+$  ions rather slowly are known as weak acids, and examples are acetic, carbonic, and boric acids. The simplest way to determine if an acid is strong or weak is to titrate it with a base and record the pH change (Figure 6.2). If near neutrality pH abruptly rises from a very low to a very high value, the acid is strong. On the other hand, if the pH change is gradual, the acid is weak. The rate of release of  $\text{H}^+$  ions is measured by the dissociation constant of an acid. Dissociation constants of some acids are given in Table 6.1.

## 6.2. THE pH CONCEPT

Weak acids release few  $\text{H}^+$  ions; the  $\text{H}^+$  ion activity (measured as moles per liter) may typically be about  $0.0001\text{ M}$  or even less. Writing such values



**Figure 6.1A. Soil pH and relative plant nutrient availability — the wider the bar, the greater the plant availability. (From Rasnake, M. 1973. University of Kentucky, College of Agriculture, Cooperative Service. AGR-19, p. 2.**



4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0  
**B**

**Figure 6.1B.** (From Brady. *The Nature and Properties of Soils*, 11th ed., © 1990. With permission of Pentice-Hall, Inc., Upper Saddle River, N.J.)

of  $\text{H}^+$  ion activity could be very cumbersome. Sorenson, a Swedish chemist, therefore developed the concept of pH, which is the logarithm of the reciprocal of the  $\text{H}^+$  ion activity.\* Thus

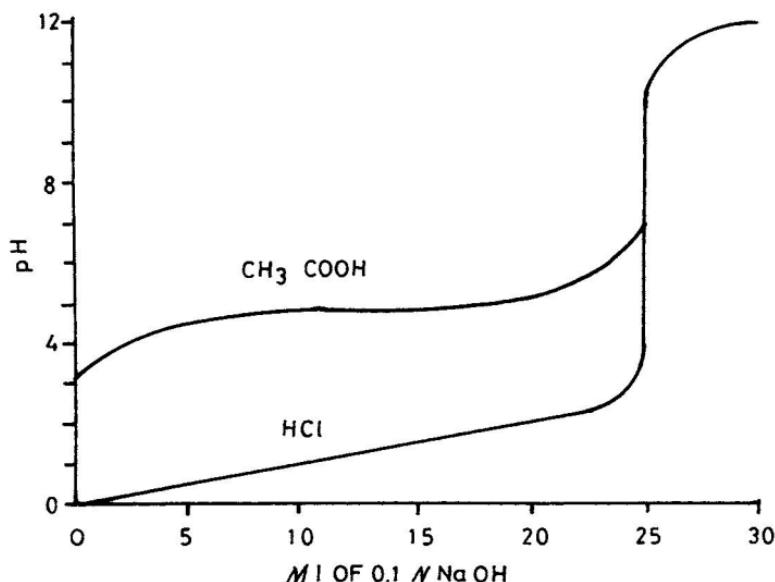
$$\text{pH} = \log \frac{1}{\text{aH}^+} = \pm \log \text{aH}^+$$

where  $\text{aH}^+$  is the hydrogen ion activity in moles per liter.

### 6.3. DETERMINATION OF SOIL pH

Soil pH is generally determined in soil slurries with soil to water ratios of 1:1 to 1:2.5. For example, 10 g of soil is added to 10 ml of distilled water in a beaker and stirred. The pH is then recorded with a pH meter (with a glass

\* The best way to understand this concept is to prepare 0.0001 M and 0.00001 M solutions of HCl and determine their pH on a pH meter. pH values recorded will be very near theoretical values of 4 and 5.



**Figure 6.2.** Titration of 0.10 N CH<sub>3</sub>COOH and 0.10 N HCl with 0.10 N NaOH. (From Tisdale et al., 1993. *Soil Fertility and Fertilizers*, 5th ed., p. 366. With permission of Prentice-Hall, Inc., Upper Saddle River, NJ.)

**Table 6.1 Ionization Constants of Some Acids**

Acid	K <sub>a</sub>	pK <sub>a</sub> <sup>a</sup>
Formic	1.772 × 10 <sup>-4</sup>	3.75
Acetic	1.754 × 10 <sup>-5</sup>	4.76
Propionic	1.336 × 10 <sup>-5</sup>	4.87
<i>n</i> -Butyric	1.515 × 10 <sup>-5</sup>	4.82
Lactic	1.374 × 10 <sup>-4</sup>	3.86
Carbonic <sup>b</sup>	K <sub>2</sub> 4.69 × 10 <sup>-11</sup>	10.33
Boric	5.79 × 10 <sup>-10</sup>	9.24
Phosphoric	K <sub>1</sub> 7.516 × 10 <sup>-3</sup> K <sub>2</sub> 6.226 × 10 <sup>-8</sup>	2.12 7.21
Sulfuric	K <sub>2</sub> 1.01 × 10 <sup>-2</sup>	2.00

$$^a \text{pK}_a = \log K_a; K_a = \frac{aH^+ aA^\pm}{aHA}$$

<sup>b</sup> Carbonic and sulfuric acids have two H<sup>+</sup> to release; K<sub>2</sub> refers to the dissociation constant of the second H<sup>+</sup>.

From Daniels and Alberti, 1967. *Physical Chemistry*, 3rd ed., p. 767. With permission of John Wiley & Sons, Inc.)

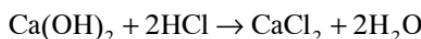
and a calomel electrode or a combined electrode) before the suspension settles. If the soil to solution ratio is increased to 1:5 or 1:10, the pH value will normally increase if the pH recorded in a 1:1 suspension is less than 6.5. However, if the pH in 1:1 soil to solution ratio was 8.5 or above (as in alkali soils), the value recorded in 1:5 or 1:10 soil to solution ratio would decrease. The reason that the pH in acid soils goes up on increasing the soil to solution ratio is because the released H<sup>+</sup> ions are distributed in a larger volume of water (dilution effect). On the contrary, the concentration of Na<sup>+</sup> (and associated OH<sup>-</sup> ions) present in alkali soils goes down on increasing soil to solution ratio and the pH value is lowered.

To overcome this variation in determining soil pH due to change in soil to solution ratio, pH may be determined in 1 M KCl or 0.01 M CaCl<sub>2</sub> solution. Such strong electrolytes (KCl or CaCl<sub>2</sub>) bring more exchangeable H in solution, and the pH value determined is generally 0.5 to 1.0 less than in aqueous suspensions. Data on the lowering of soil pH as affected by its determination in some electrolyte solutions, vis-a-vis determination in 1:1 soil to water ratio for some acid soils from Andaman Island, India, are given in [Table 6.2](#). pH determined in electrolyte solutions does not change due to an increase in soil to solution ratio. It should therefore be clearly understood that soil pH values depend very much upon how they are determined.

Although the use of KCl or CaCl<sub>2</sub> solutions reduces variation in soil pH measurement, the fact remains that in nature crop plants growing on soils encounter pH values determined in soil-water suspensions. This variability in soil pH has practical applications in crop production. This is at least one reason why rice grows well on acid sulfate soils, where the pH as determined in the laboratory is 5.0 or less. Due to submerged conditions under which rice is grown there is considerable dilution of H<sup>+</sup> ions in the soil solution and therefore the soil pH encountered by rice roots under field conditions is increased. Similarly, rice grows well on submerged alkali soils. The effect of submergence on the pH of some soils is shown in [Figure 6.3](#). This would explain why soil acidity did not receive much attention in several regions of the world where acid soils exist but lowland rice is the main crop.

#### 6.4. ACTIVE AND POTENTIAL ACIDITY

When an acid soil is suspended in water and pH is determined, one can calculate the concentration of H<sup>+</sup> ions present in the soil at that point and at that water content. For example, if the pH is 4.0 and the soil water content is 20%, one can determine H<sup>+</sup> ions present in the soil as shown below:

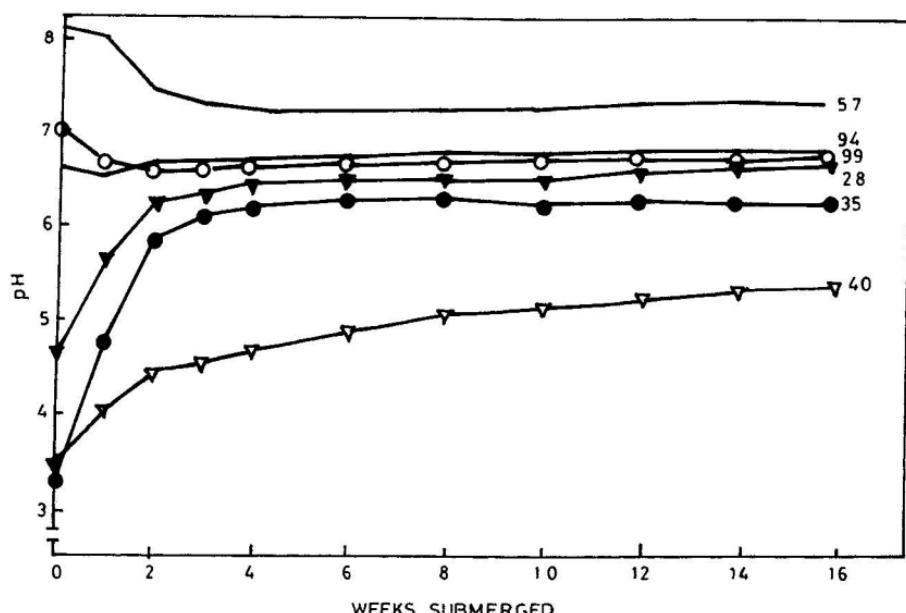


where  $2.2 \times 10^6$  kg is taken as the weight of a surface (0 to 15 cm) furrow slice of soil on one hectare of land.

Table 6.2 Changes in pH Values in Different Electrolyte Solutions

Location/soil group	pH in H <sub>2</sub> O	KCl	Change in pH from pH H <sub>2</sub> O in different electrolyte solutions		
			KNO <sub>3</sub>	K <sub>2</sub> SO <sub>4</sub>	KH <sub>2</sub> PO <sub>4</sub>
School Line (Tropfluvents)	5.5	-0.8	0.9	-0.5	-0.8
Garacharma (Troporthents)	4.4	-0.4	0.5	-0.5	-1.9
Pahargaon (Troporthents)	4.6	-0.8	0.9	-0.6	-1.4
Rangachang (Fluventic Quartzipsammements)	6.3	-0.2	0.2	-0.8	-0.4
Tushnabad (Umbric Fluventic Haplaquepts)	6.2	-1.5	1.9	-1.0	-0.3
Wandoor (Fluventic Dystrochrepts)	5.5	-1.7	-1.9	-0.3	-0.7
Shoal Bay - 9 (Fluventic Dystrochrepts)	5.0	-1.2	1.4	+0.3	-1.0
Shoal Bay -12 (Fluventic Dystrochrepts)	5.2	-1.3	1.3	+0.2	-1.0
Shoal Bay -19 (Fluventic Dystrochrepts)	4.9	-0.9	1.0	-1.2	-1.0
Manarghat (Troporthents)	4.9	-1.3	1.0	-0.7	-1.4
Paithankhari (Fluventic Sulfaquents)	4.9	0.8	0.9	0.8	-1.3
Chouldari (Tropofluvents)	5.8	-1.3	1.2	-0.8	-0.4
Sipighat (Troporthents)	4.6	-0.7	0.9	-0.5	-1.7
Guptapara (Tropofluvents)	5.8	-1.5	1.2	-0.6	-0.5
Wandoor (New) (Fluventic Dystrochrepts)	5.2	-0.4	0.4	-0.5	-0.6

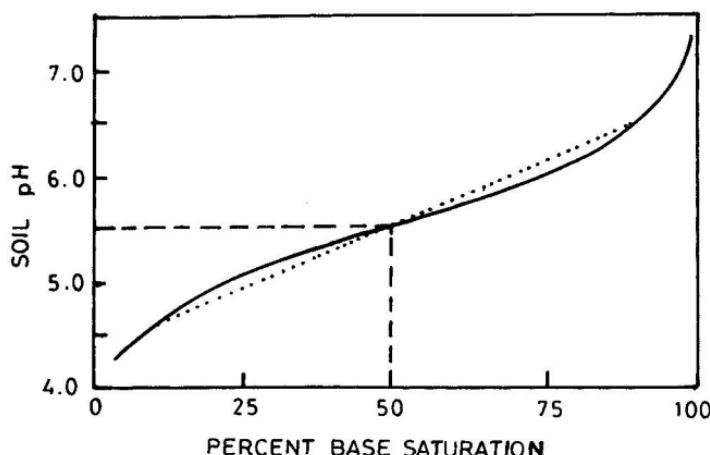
From Mongia and Bandypadhyay, 1991. J. Indian Soc. Soil Sci. 39:351–354. With permission.



Soil No.	Texture	pH	O.M. %	Fe %	Min %
28	clay	4.9	2.9	4.70	0.08
35	clay	3.4	6.6	2.60	0.01
40	clay	3.8	7.2	0.08	0.00
57	clay loam	8.7	2.2	0.63	0.07
94	clay	6.7	2.6	0.96	0.09
99	clay loam	7.7	4.8	1.55	0.08

**Figure 6.3. Kinetics of the solution pH of six submerged soils. (After Ponnamperuma, 1976. *The Fertility of Paddy Soils and Fertilizer Applications for Rice, Food and Fertilizer Technology Centre for the Asian and Pacific Region, Taipei, Taiwan.* pp. 1–27.)**

A very small amount of base would be needed to neutralize this acidity. However, when neutralized, the soil will still record essentially the same pH value. This occurs because more  $H^+$  ions will be released by soil to maintain equilibrium. Soil has much more stored  $H^+$  ions than is determined by measuring soil pH. Such stored acidity is known as “potential acidity,” while the acidity determined as soil pH is termed as “active acidity.” This behavior of acid soils is similar to that of weak acids, which also have much more potential acidity than the active acidity. This is why there is no sharp end point in the titration of acid soils with bases (Figure 6.4). On the other hand, potential and active acidity in strong acids is nearly the same.



**Figure 6.4. Theoretical titration curve for a large number of Florida soils. The dotted line indicates the zone of greatest buffering. The maximum buffering should occur at approximately 50% base saturation. (From Peech, 1941. *Soil Sci.* 51:473–486. With permission of Williams & Wilkins, Baltimore, MD.)**

## 6.5. BUFFERING CAPACITY

Buffers are systems that maintain their pH within a narrow range; that is, they resist a change in pH on addition of small amounts of acid or base. Mixtures of weak acids and their salts are used to make buffers. For example, acetic acid–sodium acetate, ammonium hydroxide–ammonium chloride and phosphoric acid–sodium phosphate are frequently used buffers. In the acetic acid–sodium acetate buffer, the salt sodium acetate dissociates and gives rise to a large concentration of acetate ions, which suppress the dissociation of acetic acid. If small quantities of an acid such as HCl are added, excess acetate ions in the buffer react with H<sup>+</sup> ions and form acetic acid, and there is no change in pH. Similarly, if small amounts of NaOH are added, hydroxyl ions are neutralized by H<sup>+</sup> ions in solution. When this happens more H<sup>+</sup> ions are released by the dissociation of acetic acid. Thus the buffer resists a change in its pH. Acid soils also react in a similar manner, and the change in their pH requires application of large amounts of a base (lime). Also, a sufficient time interval has to be provided to affect a pH change. Such soils are said to have a large buffering capacity.

The buffering capacity of a soil is related to its cation exchange capacity (CEC) and is therefore related to the clay content and mineralogy and to the amount of soil organic matter present. The larger the amounts of either clay or organic matter, the greater the buffering capacity.

## 6.6. NATURE OF SOIL ACIDITY

Initially, soil acidity was identified with humic acids. However, it was soon discovered that leaching acid soils with neutral salt solutions produced

**Table 6.3 Total Acidity and Exchangeable  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{H}^+$  in the 1 N  $\text{BaCl}_2$  Leachates of H-Clays (cmol kg<sup>-1</sup>)**

Soil	Total acidity	Exchangeable $\text{Al}^{3+}$	Exchangeable $\text{Fe}^{3+}$	Exchangeable $\text{H}^+$
Satara F	63.4	44.4	0.5	18.5
Jorhat F	23.3	12.5	0.4	10.4

From Mukherjee et al., 1947. J. Colloid Sci. 1:247–254. With permission of Academic Press, Inc.

extracts that could be titrated for acidity. These leachates contained sizable amounts of Al (Table 6.3), and exchangeable Al was identified as the main cause of soil acidity. Although these results were obtained by several earlier workers such as T.B. Veitch in the United States, C.E. Marshall and R.K. Schofield in the United Kingdom, H. Riehm in Denmark, and V.A. Chernov in the USSR (Jenny, 1961), the subject received considerable attention only later (Lin and Coleman, 1960; Shoemaker et al., 1961; Kamprath, 1970; and Sanchez, 1976). McLean et al. (1965) observed that various forms of soil acidity appear to have the following order of activity: exchangeable or permanent charge  $\text{H}^+$  > exchangeable or permanent charge  $\text{Al}^{3+}$  > hydroxy - Al monomers > hydroxyl Al polymers  $\approx$  organic matter acidity  $\approx$  lattice Al-OH or Si-OH acidity. Brady (1990) suggested the term residual acidity for acidity not determined by active acidity and the term exchangeable or titratable acidity for acidity extracted by KCl. Titratable acidity determined by KCl was much less than that determined by ammonium acetate at pH 4.8, using Shoemaker-McLean-Praftt (SMP) buffer, Woodruff buffer, and Mehlich buffer (Table 6.4) (McLean et al., 1964).

As already brought out in Chapter 4, soils contain a permanent negative charge (permanent acidity) due to isomorphous substitution in clay minerals. They also acquire negative charges with an increase in soil pH (pH-dependent acidity) due to hydroxyl ions on the edges of the clay and those associated with hydroxides and oxyhydroxides of iron and aluminum. Furthermore, data from Ohio soils (Table 6.5) varying in organic matter content show that soil organic matter can largely affect the permanent negative charge and total cation exchange capacity of soils; the effect on pH-dependent CEC was much less. Because the negative charge on soil organic matter is due to -OH and -COOH radicals, the contribution of exchangeable  $\text{H}^+$  on soil acidity in organic matter rich soils could be considerable. Data in Table 6.5 also show that liming can considerably reduce pH dependent CEC.

## 6.7. FACTORS AFFECTING SOIL ACIDITY

A number of factors affect soil acidity. These include (1) the kind of chemical fertilizer used; (2) the amount of basic cations removed by the crop plants; (3) leaching of cations; (4) organic residues and their decomposition;

**Table 6.4** Soil Acidity, as Indicated by Various Methods, and Cation-Exchange Properties of Four Representative Ohio Soils

Soil Type	pH	Extr. Al (NH <sub>4</sub> OAc- pH 4.8) (me/100 g)	Soil Acidity (cmol kg <sup>-1</sup> )						CEC (cmol kg <sup>-1</sup> )		
			CaCO <sub>3</sub> incub. pH 6.8	KCl exch. pH 6.8	SMP buffer	Mehlich buffer	Woodruff buffer	Direct titration pH 6.8	pH 8.1	NH <sub>4</sub> O Ac pH 7.0	BaCl <sub>2</sub> pH 4.1
Bennington si.l	4.5	1.5	9.4	1.6	7.2	9.8	4.4	6.4	12.0	11.0	13.1
Mahoning si.l	4.2	3.7	16.8	4.4	16.0	19.0	10.0	13.0	26.0	13.2	16.5
Ashtabula si.l	4.7	7.8	17.0	4.4	17.2	18.2	11.4	10.0	21.0	17.0	20.0
Trumbull si.l	4.0	5.9	21.8	6.0	19.6	20.6	10.6	17.0	33.0	14.4	19.0

From McLean et al., 1964. Soil. Sci. 97:120. With permission of Williams & Wilkins, Baltimore, MD.

**Table 6.5 The Amount of Permanent Charge (KCl-CEC), pH-Dependent CEC and Total CEC with or without Organic Matter in Some Ohio Soils Differing in Organic Matter Content**

Soil	Lime added (cmol kg <sup>-1</sup> )	Soil pH	Organic matter (%)	KCL-CEC (cmol kg <sup>-1</sup> )		pH-dependent CEC (cmol kg <sup>-1</sup> )		Total CEC (cmol kg <sup>-1</sup> )	
				OM	WOM	OM	WOM	OM	WOM
Clermont	4	5.7	1.4	6.4	4.9	3.8	2.4	10.2	7.3
	8	7.2	—	8.2	5.5	1.9	2.9	10.1	8.4
Bennington	0	4.8	2.4	7.3	6.4	10.7	4.6	18.0	11.0
	8	6.2	—	11.1	7.3	5.6	4.3	16.7	11.6
Fries	8	4.9	4.2	9.9	9.8	16.5	9.0	26.4	11.2
	20	6.6	—	16.6	10.6	3.3	6.6	19.5	11.3
Cambridge	0	4.4	9.7	10.9	7.3	31.1	7.8	42.0	11.9
	45	7.0	—	24.4	8.5	8.5	6.0	32.9	9.7

*Note:* OM, with organic matter; WOM, without organic matter.

Adapted from McLean et al. (1965).

**Table 6.6 Effect of Forms of Chemical Fertilizer on the pH of Surface (0–5 cm) Soil**

Fertilizer	N rate	pH 1:1 (H <sub>2</sub> O)		
		Alfisol	Ultisol	Oxisol
Control	0	6.09	4.92	3.87
AS <sup>a</sup>	100	4.02	3.98	3.51
urea	100	4.24	4.18	3.46
CAN <sup>b</sup>	100	4.64	4.60	3.47

<sup>a</sup> Ammonium sulfate.

<sup>b</sup> Calcium ammonium nitrate.

From Stumpe and Vlek, 1991. *Soil. Sci. Soc. Am. J.* 55:150. With permission of the Soil Science Society of America, Madison, WI.

(5) nitrogen transformations; and (6) deposition of nitrate, sulfate, and acid-forming chemicals by rain.

### 6.7.1. Chemical Fertilizers

Chemical fertilizers are well known for their acidity and basicity-forming effects. The basicity-forming effect of Chilean nitrate ( $\text{NaNO}_3$ ) was one of the factors that made it popular in the early days of farming when fertilizers first appeared. Both nitrogen and phosphorous fertilizers are known for these effects.

In an experiment in the United States at the International Fertilizer Development Center (IFDC) in Alabama, studies were made in plexiglass cylinders (5 cm internal diameter and 70 cm length) with three soils; an alfisol from Egdeba, southwestern Nigeria; an ultisol from Onne, southeastern Nigeria; and an oxisol from Carimagua, eastern Colombia. Following each application of N at rates of 0, 50, 100  $\text{kg ha}^{-1}$  as urea, ammonium sulfate, or calcium ammonium nitrate, the soils were flushed with distilled water 30 times during 2 years of study with 6-week rest periods after each five cycles. The pH values recorded after the study are given in Table 6.6. Application of fertilizer N reduced soil pH in all three soils. In the alfisol, as well as in the ultisol, the reduction in soil pH was the most with ammonium sulfate and the least with calcium ammonium nitrate. The differences between the N sources were not distinct in the oxisol.

Data on changes in soil pH due to fertilizer application from long-term experiments on acid Indian soils are given in Table 6.7. These data confirm that continuous application of N results in depletion of soil pH. Application of lime stopped this depletion in soil pH.

A method for determining the acidity or basicity of fertilizers was developed by Pierre in 1933. The basic assumptions in this method are as follows:

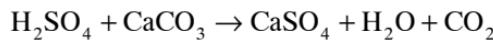
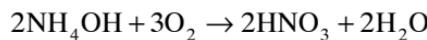
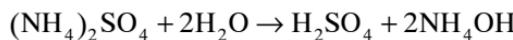
**Table 6.7 Changes in Soil pH as Affected by Intensive Manuring and Cropping on Acidic Soils in India (1988–1989 Data)**

Treatments	Ranchi (Haplustalf)	Palampur (Hapludalf)
Control	5.3	5.6
Nitrogen	4.4	4.9
NPK + lime	5.8	6.6
LSD (0.05)	0.07	0.2
Initial (1971) value	5.3	5.8

From Nambiar et al. 1992. Annual Report, (ICAR) Indian Agricultural Research Institute, New Delhi, p. 151.

1. The acid-forming effect of fertilizer is caused by all of the contained sulfur and chlorine, one-half of the nitrogen, and one-third of the phosphorous. However, Andrews (1954) maintained that the entire amount of N contributed to soil acidity.
2. The presence of calcium, magnesium, potassium, and sodium in fertilizer raises the pH of the soil.

Using the above assumption let us calculate equivalent acidity for ammonium sulfate  $(\text{NH}_4)_2\text{SO}_4$ . When ammonium sulfate is applied to soil, the following reactions will occur:



Thus if all nitrogen is considered to be responsible for causing soil acidity (as proposed by Andrews), each molecule of ammonium sulfate (containing 28 g N) will require two molecules of calcium carbonate ( $2 \times 100$  g). Thus 28 g N will react with 200 g CaCO<sub>3</sub>. This is equal to 7.14 kg calcium carbonate (lime) per kg N in fertilizer (Column 3 of Table 6.8). If only half of the nitrogen contributes to soil acidity (as per Pierre), then each molecule of ammonium sulfate will react with 1.5 molecules of calcium carbonate (0.5 molecule for N, 1 molecule for sulfate). Thus 28 g N will react with 150 g CaCO<sub>3</sub>. This is equal to 5.35 kg calcium carbonate (lime) per kg N (Column 5 of Table 6.8). Amounts of lime needed per 100 kg fertilizer material can be easily calculated by multiplying by the percentage of N (or other nutrient) in the fertilizer material. For ammonium sulfate the values obtained will be  $7.14 \times 20.5 = 146$  (Column 4 of Table 6.8) or  $5.35 \times 20.5 = 110$  (Column 6 of Table 6.8) using

**Table 6.8 Equivalent Acidity and Basicity of Chemical Fertilizers**

Chemical fertilizer	Percent N	Lime required to neutralize acidity			
		Andrews		Pierre <sup>a</sup>	
		Per kg N	Per 100 kg fertilizer	Per kg N	Per 100 kg fertilizer
1	2	3	4	5	6
<b>Nitrogen fertilizers</b>					
Ammonium sulfate	20.5	7.14	146	5.35	110
Anhydrous ammonia	82.2	3.57	293	1.80	148
Calcium ammonium nitrate	20.5	1.77	36	0	0
Urea	46.6	3.57	166	1.80	84
Urea - ammonia liquor	45.5	3.57	162	1.80	82
<b>Phosphate fertilizers</b>					
Ammonphos A	11.0	6.77	74	5.00	55
Di-ammonphos (18-46-0)	18	—	—	—	—
Ordinary super-phosphate	0	0	0	0	0
Triple super-phosphate	0	0	0	0	0
<b>Potash fertilizers</b>					
Muriate of potash	0	0	0	0	0
Sulfate of potash	0	0	0	0	0

<sup>a</sup> Now official method in the United States.

Andrews or Pierre's assumption. Equivalent acidity or basicity of some chemical fertilizers is given in [Table 6.8](#).

### 6.7.2. Removal of Basic Cations

All plants take up exchangeable bases during their growth. When they are completely or partly removed from the land, the net result is loss of bases from the soil, and this leads to the development of soil acidity. This has been clearly brought out from data from the long-term experiments conducted in various countries. Crops differ in the quantity of bases removed. For example, leguminous crops remove more calcium and less potassium than cereals.

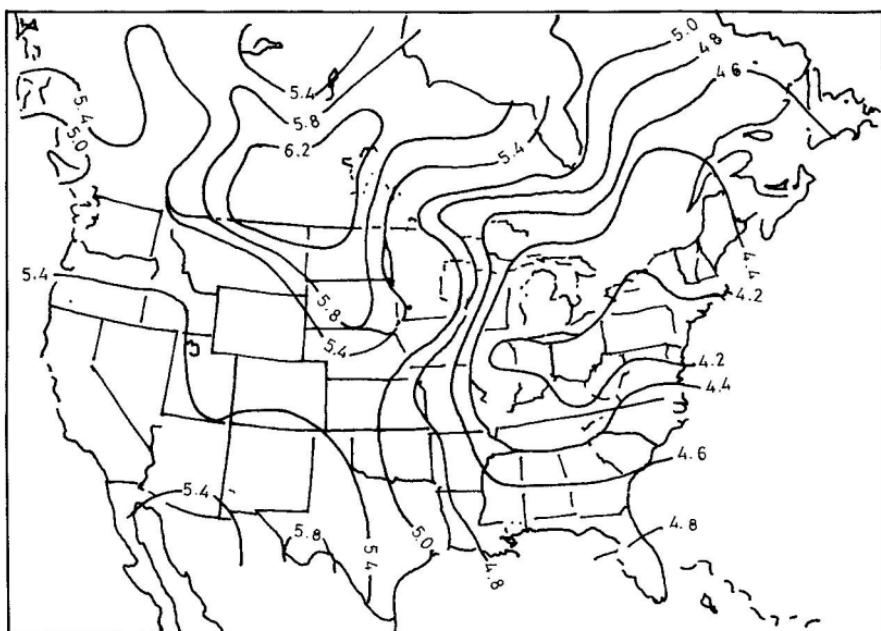
Pierre and Banwart (1973) suggested that the ratio of excess bases (EB) defined as total cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) minus total anions ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ , and  $\text{H}_2\text{PO}_4^-$ ) in the plant material to plant nitrogen content as the criterion for determining the acid-forming property of crops. Crop plants with EB:N ratios above 1.0 increase soil acidity, while those below 1.0 decrease acidity. In their study of 149 samples taken at different stages of growth of 26 crop species, only buckwheat, tobacco, and spinach had values slightly above 1.0. Cereal and grasses had average ratios of 0.43 and 0.47, respectively, meaning thereby that only 43 and 47%, respectively, of the nitrogen they received was acid forming.

### 6.7.3. Nitrogen Transformations

When ammonium or ammonium-forming N fertilizers are applied to soils, little to large amounts of N can be lost by ammonia volatilization (see [Chapter 8](#)). This lost N does not contribute to nitrate formation and the resultant acidity. Similarly, the amount of N lost as  $\text{N}_2$  or  $\text{N}_2\text{O}$  due to denitrification (see Chapter 8) also does not contribute to soil acidity. Whatever the  $\text{NH}_4^+$  source, nitrification is an acidic process.

### 6.7.4. Acids Brought in by Rain

A number of gaseous sulfur and nitrogen compounds, especially  $\text{SO}_2$  and  $\text{NO}_2$ , are emitted into the atmosphere through natural processes and/or by man's activities. These gaseous compounds are dissolved in rains, come down to earth, and are added to soil. A study in Alberta (Lau and Das, 1985) showed that about  $8.8 \text{ kg ha}^{-1}$  of sulphate,  $4 \text{ kg ha}^{-1}$  of nitrate, and  $0.15 \text{ kg ha}^{-1}$  of hydrogen were added annually to the soil. Acid rain occurs at many places in the world, and in the United States it exhibits a maximum in the northeastern region and adjacent Canadian provinces. A pH contour map of North America is shown in [Figure 6.5](#). Thus acids are regularly added to soil by precipitation, the amounts being greatest near industrial towns.



**Figure 6.5. Precipitation pH contour map of North America for the period 1972–1982.** (From Mohnen and Wilson, 1985. *Acid Deposition—Environmental, Economic and Policy Issues*, D.A. Adams and W.P. Page, Eds., p. 440. With permission of Plenum Press.)

### 6.7.5. Leaching of Bases

Leaching of bases as a factor responsible for soil acidity is well established in pedogenesis.

## 6.8. SOIL pH AND CROP PRODUCTION

Crops do differ in their soil pH requirements. The optimum soil pH for crop production is generally considered to be between 6.5 and 7.0, and lime applications are made to that effect. Kamprath (1971) and his group of research workers in North Carolina have, however, shown that pH values greater than 6.0 or 6.2 may not only be unnecessary but harmful. On oxisols and ultisols of the warm, humid, southeastern United States they have suggested liming soils sufficient to reduce exchangeable  $\text{Al}^{3+}$  to less than 10% of the effective CEC (Kamprath, 1970). On the other hand, liming to pH values of 6.5 to 6.8 is recommended for alfisols and mollisols, such as in the midwestern United States (Tisdale et al., 1985).

The chemical and physical properties of oxisols and ultisols in the southern United States are largely controlled by hydroxyaluminum and hydroxyiron coatings on clay fraction. These coatings, on liming, become pH-dependent

adsorption sinks for P, Zn, Mg, and other elements. This would explain why a lower pH value is considered suitable for general field crops on ultisols and oxisols than in alfisols and mollisols.

Liming oxisols and ultisols to pH 7.0 reduces phosphorous and micronutrient uptake by crops, reduces water percolation, and subsequently reduces plant growth (Kamprath, 1971). Grove and Sumner (1985) working on an ultisol (Typic Hapludult—Bradson clay loam) in Georgia showed that lime application at some point induced magnesium stress in corn (Figure 6.6). There was also a depression in plant zinc concentration.

Aluminum toxicity is probably the major limiting factor to plant growth and crop production in strongly acidic soils (Foy, 1992). The root system of plants is adversely affected by Al-toxicity (Figure 6.7). In cereals roots appear corolloid with many stubby lateral roots and no fine branching. This limits plants ability to absorb water and nutrients and results in poor growth. Crops and cultivars among a crop differ in tolerance to Al-toxicity, and research is going on to identify such cultivars for increasing crop production in acidic soils.

## 6.9. LIME REQUIREMENT

Due to the buffering capacity of soils, change in pH takes considerable time. Therefore the ideal procedure for determining lime requirement would be mixing a known amount of soil with different amounts of lime ( $\text{CaCO}_3$ ) for a fairly long period (Figure 6.8) and then determining the amount of lime required to obtain the desired pH. This procedure, however, requires a fairly long time, so is not suitable for soil-testing purposes. Advantage has been taken of buffer solution simulation of acidic soils. A number of buffer solutions have been proposed for determining the lime requirement of soils. Some of these are: p-nitrophenol buffered at about pH 7 (Schofield, 1933); barium chloride-triethanolamine at pH 8 (Peech et al., 1947); p-nitrophenol, potassium dichromate, calcium acetate-MgO buffered at pH 7 (Woodruff, 1948); and p-nitrophenol-triethanolamine-potassium chromate-calcium acetate, and calcium chloride buffer adjusted to pH 7.5 with NaOH (Shoemaker et al., 1961); the Schomaker-McLean-Pratt (SMP) buffer has found most favor with United States soil scientists. Lime requirements of some acidic Indian soils, as determined by  $\text{CaCO}_3$  incubation (for one month), Peech's buffer, SMP buffer, and Schofield buffer, are given in Table 6.9 (Dolui and Saha, 1984). Values determined by Peech and Schofield buffers were very high, while those determined by SMP buffer were closest to results from the  $\text{CaCO}_3$  incubation procedure. The correlation coefficients ( $\gamma$ ) between  $\text{CaCO}_3$  incubation and the Peech, SMP, and Schofield buffers were 0.917, 0.932, and 0.749 and were significant. The SMP buffer is especially well suited for soils possessing the following properties: lime requirement  $> 4 \text{ cmols kg}^{-1}$  ( $> 4400 \text{ kg lime ha}^{-1}$ ; taking the weight of 0 to 15 cm surface soil layer weight at  $2.2 \times 10^6 \text{ kg ha}^{-1}$ ), pH  $< 5.8$ , organic matter concentration of  $< 10\%$  and appreciable quantities of soluble

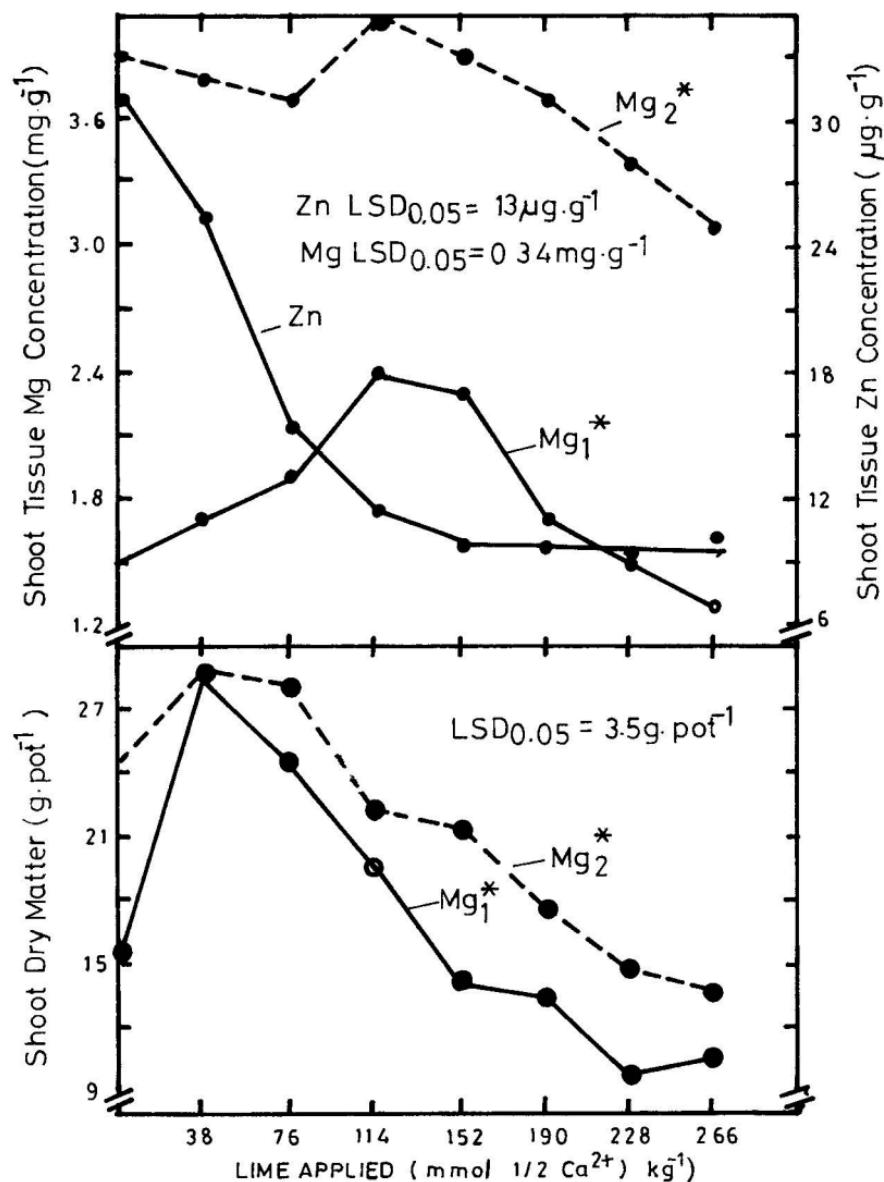


Figure 6.6. Relationships between shoot dry matter productivity, shoot tissue Mg, Zn, concentrations, and lime application rate.  $^* \text{Mg}_1, \text{Mg}_2 = 2, 10 \text{ mmol (1/2 Mg}^{2+} \text{)} \text{ kg}^{-1}$ , respectively. (From Grove and Sumner, 1985. *Soil Sci. Soc. Am. Proc.* 61:428–432. With permission of the Soil Science Society of America, Madison, WI.)

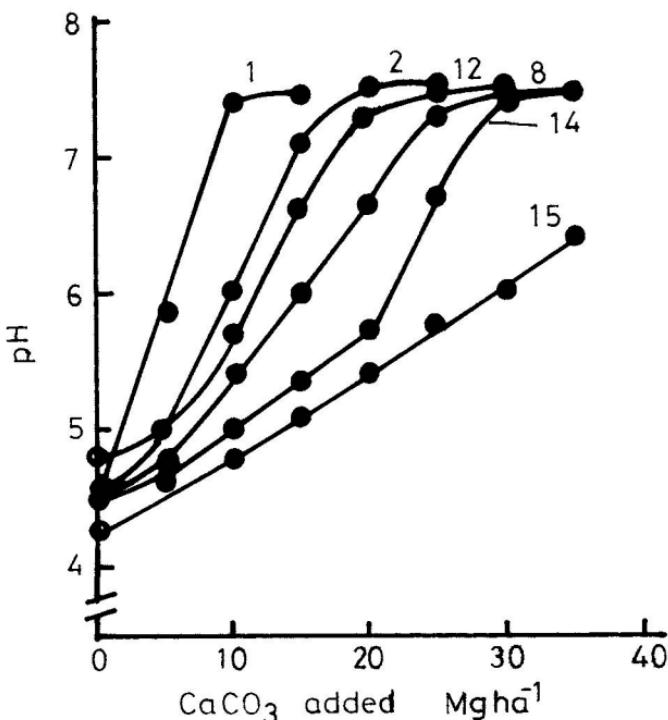


**Figure 6.7. Al-toxicity — cotton plants grown on 0, 0.75, 1.5, 3.0, and 6.0 mg Al L<sup>-1</sup>. (Photo courtesy of Dr. C. Foy, USDA, Maryland.)**

(extractable) Al (Tisdale et al., 1985). However, the SMP buffer will give lime requirement values that frequently result in overliming of many low-base-status soils.

On highly leached tropical soils, namely, ultisols and oxisols, there is a considerable amount of pH-dependent charge due to hydroxides of Al and Fe. The lime requirement determined by buffers such as the SMP buffer could be very high. Research with these soils (Sanchez, 1976) has suggested that exchangeable Al<sup>3+</sup> determination is a better criterion for determining lime requirement for these soils. Exchangeable Al<sup>3+</sup> can be determined by extracting soils with unbuffered 1 N KCl (Lin and Coleman, 1960). There is very little exchangeable Al<sup>3+</sup> when soil pH is 5.5 or above (Figure 6.9). However, when Mn toxicity is suspected, liming may be done to raise the pH up to 6.0. The generally suggested lime application on ultisols and oxisols is that which provides sufficient lime to neutralize soil acidity to 20 to 25% Al saturation. Al saturation is calculated by dividing exchangeable Al<sup>3+</sup> (and exchangeable H<sup>+</sup> if present) by the sum of exchangeable bases plus exchangeable Al<sup>3+</sup> (and H<sup>+</sup>). The relationships between percent Al saturation and soil pH in ultisols and oxisols of Puerto Rico is shown in Figure 6.10.

Liming ultisols and oxisols to pH 5.5 or 6.0 is suggested (Sanchez, 1976) when manganese toxicity is suspected. Kamprath (1970) suggested that the lime requirement be determined by multiplying exchangeable Al<sup>3+</sup> (cmol kg<sup>-1</sup>)



**Figure 6.8.** Titration curves for some Ohio soils. pH after 17 months of moist incubation with lime. Number on curves indicates different soils. (From Shoemaker et al., 1961. *Soil Sci. Soc. Am. Proc.* 25:274–277. With permission of Soil Science Society of America, Madison, WI.)

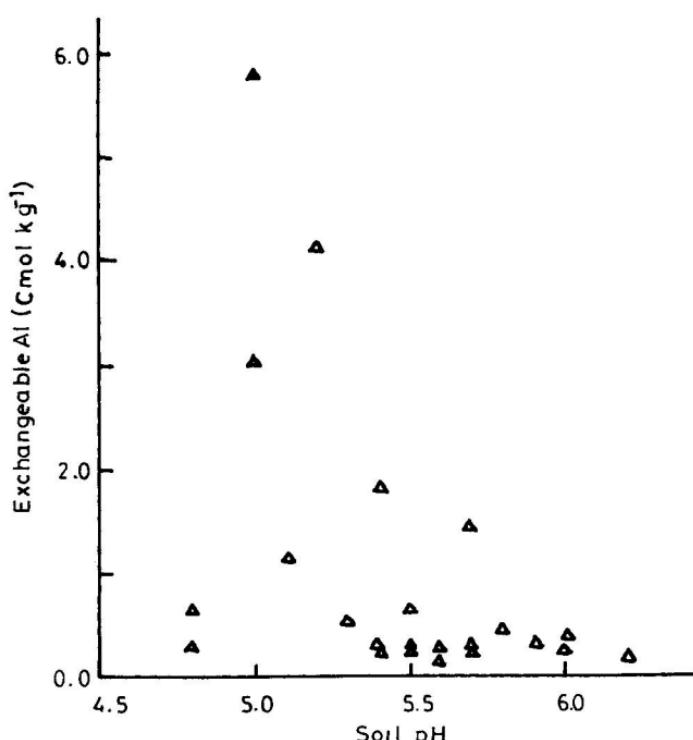
by 1.5 to give the  $\text{cmol kg}^{-1}$  of Ca or  $1.65 \text{ cmol kg}^{-1}$  of  $\text{CaCO}_3$ . This amount of lime would neutralize 85 to 90% of exchangeable  $\text{Al}^{3+}$  in soils containing 2 to 7% organic matter; for soils containing more organic matter, the factor may be raised to 2 to 3. Application of this concept of liming has substantially reduced the rates of lime applied to soils.

Another important component of the lime requirement is the level of exchangeable  $\text{Al}^{3+}$  that specific crops can tolerate; cotton, sorghum, and alfalfa are susceptible to levels of 10 or 20% Al-saturation, while corn is sensitive to 40 to 60% Al-saturation (Sanchez, 1976) (Figure 6.11). Thus cotton, sorghum, and alfalfa fields need to be limed to nearly zero Al-saturation level, while liming corn fields to 20% Al-saturation is adequate. Crops such as rice (explained earlier), coffee, pineapple, and some pasture species seldom respond to liming even in soils with high Al-saturation. In a recent study on ultisols and inceptisols in Nigeria (Nwachukwu and Loganathan, 1991), near maximum corn yield was obtained when liming reduced Al-saturation to 25%. No increase in corn yield was obtained by liming beyond pH 5.5.

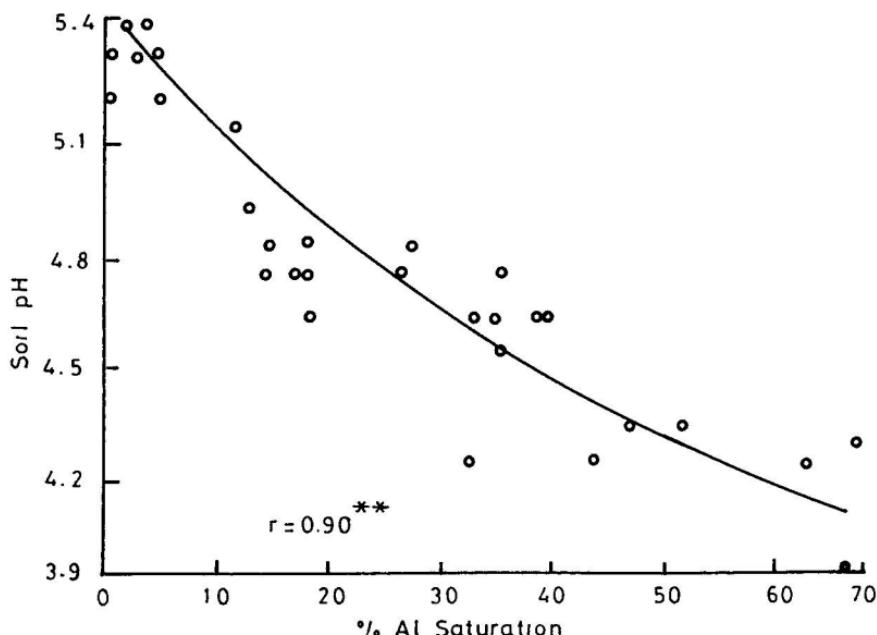
**Table 6.9 Lime Requirement ( $Mg\ ha^{-1}$ ) by Calcium Carbonate Incubation and Other Diagnostic Methods**

Location	Incubation	Peech	SMP (pH 6.4)	Schofield
Bagdubi	0.39	5.93	1.72	20.92
Ausgram	0.98	11.86	3.58	20.89
Andibahara	1.28	8.15	1.72	19.55
Kalimpong	1.38	14.08	6.67	23.54
Dimrulia	1.58	8.89	4.20	17.01
Kapgari	1.97	3.70	0.49	14.39
Arambagh	2.32	8.89	3.58	26.08
Khaprail	3.95	17.79	12.84	20.86
Rajganj	5.14	22.23	10.37	24.85
Kharibari	5.93	18.53	9.76	26.16
Kalijhora	6.22	20.01	14.08	20.92
Bhutobori	18.48	33.35	23.10	32.70

From Dolui and Saha, 1984. J. Indian Soc. Soil Sci. 32:158–161.  
With permission.



**Figure 6.9. Exchangeable aluminum at different pH values in nine oxisols and andepts from Panama. (From Mendez-Lay, 1973. M.S. Thesis, North Carolina University, Raleigh.)**



**Figure 6.10.** Relationship between soil pH and aluminum saturation in eight ultisols and oxisols of Puerto Rico. (From Abruna et al., 1975. *Soil Management in Tropical America*. With permission of North Carolina University Press.)

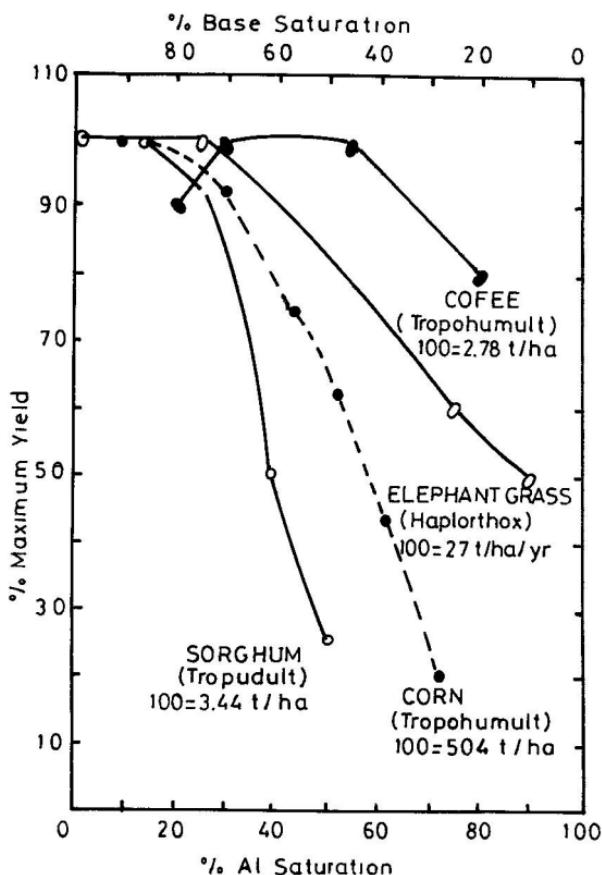
## 6.10. LIMING MATERIALS

**Limestone.** The most commonly used liming material is limestone or calcium carbonate ( $\text{CaCO}_3$ ) and all other liming materials are evaluated relative to their effectiveness compared with calcium carbonate (given a value of 100).

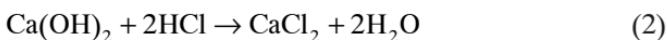
Limestone deposits are found in most countries of the world. It is often mined by open-pit methods (quarrying) using explosives to blast the rock. The broken rock pieces are crushed to sizes of 2.5 cm (1 inch) or less and further ground or pulverized to the desired size. Generally an 8- to 10-mesh\* material (more than 75% should pass the screen) is considered desirable (discussed later). The quality of commercial limestone generally used is 90 to 98% calcium carbonate equivalent (CCE), but even inferior materials may be marketed. Lower CCE values are due to its impurities such as clay.

The calcium carbonate equivalent (CCE) of a liming material is determined as shown below giving the examples of limestone ( $\text{CaCO}_3$ ) and slaked lime ( $\text{Ca(OH)}_2$ ):

\* A 10-mesh size refers to a sieve where each linear inch is divided into 10 divisions; thus there will be 100 divisions per square inch. The actual size of pores will also depend upon the thickness of the wire used to make the sieve.



**Figure 6.11. Yield responses to liming in Puerto Rican oxisols and ultisols.**  
 (From Sanchez, 1976. *Properties and Management of Soils in the Tropics*. With permission of John Wiley & Sons.)



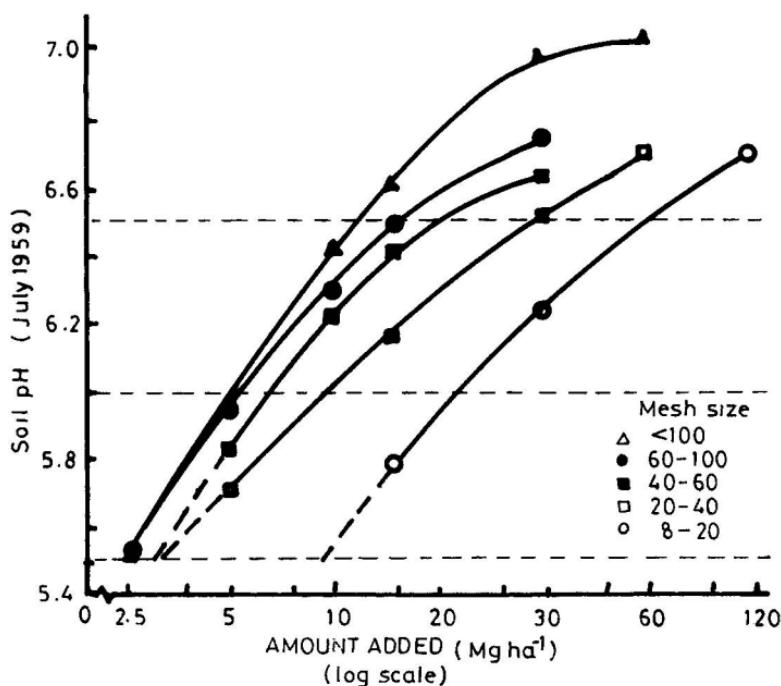
In equation 1 100 g calcium carbonate or limestone would neutralize 73 g HCl. However, the same amount of HCl is neutralized by only 74 g slaked lime as shown in equation 2. Thus 74 g slaked lime is equivalent to 100 g calcium carbonate or limestone. Therefore 100 g slaked lime would equal  $\frac{100}{74} \times 100 = 135$  g limestone or calcium carbonate; 135 is the calcium carbonate equivalent (CCE) of slaked lime.

**Calcium Oxide ( $CaO$ ).** Calcium oxide or (quick) lime is obtained by calcining limestone. Calcium oxide gives very quick results and is therefore used when rapid change in soil pH is required. Because the material is a white powder, which irritates skin and eyes, it is difficult to apply and mix in soil. After application, it forms flakes or granules in the presence of soil water. Due to reaction with atmospheric or soil carbon dioxide, calcium carbonate is formed and is deposited on the surfaces of flakes or granules. In this condition the remaining  $CaO$  remains in the soil for a fairly long time. The calcium carbonate equivalent (CCE) for calcium oxide is 179%.

**Calcium Hydroxide ( $Ca(OH)_2$ ).** This is slaked lime and is made by reacting calcium oxide with water. It is also known as builders' lime and is used for construction purposes. Calcium hydroxide is generally used for whitewashing houses in India and many other developing nations. With the passage of time calcium carbonate forms on the surface by reaction with atmospheric carbon dioxide, and the color then becomes pale yellow. This is the reason whitewashing is repeated every year. Calcium hydroxide is much easier than calcium oxide to handle and apply. The CCE value for slaked lime is 135%.

**Dolomite.** This is calcium magnesium carbonate  $[CaMg(CO_3)_2]$ . The CCE value is 109%. Dolomite has the advantage of supplying Mg as a plant nutrient and is especially important in Mg-deficient soils such as some soils developed from glacial till.

**Other Materials.** Other liming materials include marl (unconsolidated deposits of calcium carbonate frequently mixed with earth; found near sea coasts), slags (blast furnace slag, basic slag, electric furnace slag), fly ash (from coal burning in thermal power-generating plants), flue dust (from cement-manufacturing plants), sugar lime (from carbonation used in sugar factories), and pulp mill lime. In the United States and other countries, scrubbers (calcium carbonate solutions) are also used to remove  $SO_2$  and other gases from smokestacks, and precipitators are used to remove particulate matter. These materials usually have some neutralizing capacity. These and several other materials could be available as industrial wastes at throw-away prices and could be used for liming. A large number of experiments in India were conducted with basic slag as a source of phosphorous with limited success since most Indian basic slags contained only 2 to 3%  $P_2O_5$ , which was too little compared with the grinding and transportation costs. It was never tested as a liming material in India since there was no need; more than 80% of cultivated soils in India have a pH well above 7.5.



**Figure 6.12.** Effect of various rates of dolomitic limestone fractions on the pH of Withee silt loam after 2 years of equilibration under field conditions. (From Love et al., 1960. *Trans. 7th Int. Cong. Soil Sci.* 3:293-301. With permission of International Society of Soil Science, Vienna, Austria.)

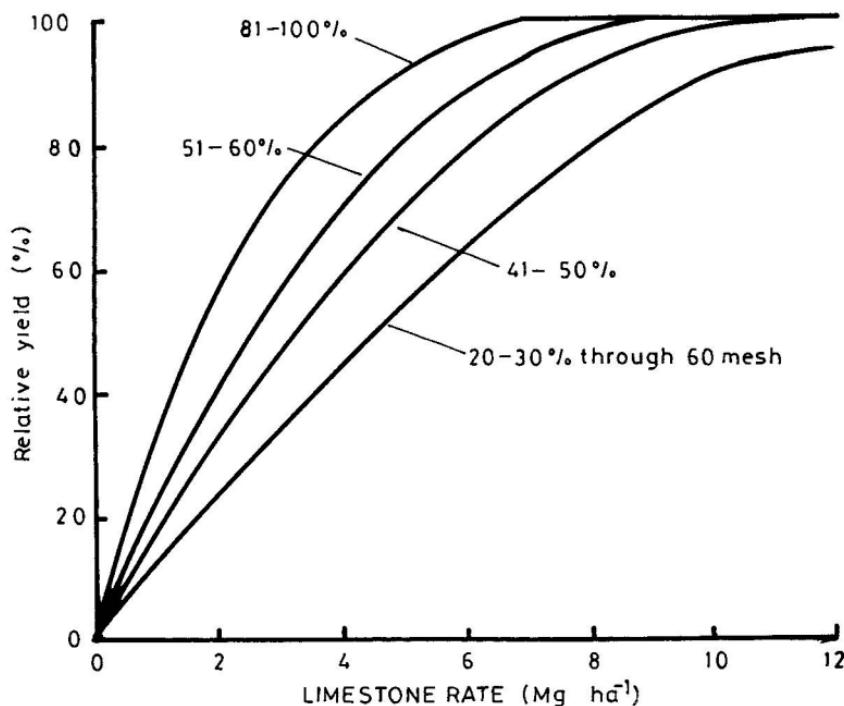
## 6.11. FINENESS OF LIMESTONE

Besides the purity of the limestone, the degree of fineness is also important; the finer the limestone, the faster it reacts. This can be reflected in soil pH changes (Figure 6.12), as well as in crop yields (Figure 6.13). Also less limestone is required to achieve the desired soil pH changes and to improve crop yields if the particle size is finer. However, finer grinding adds to the cost of material. Because lime is generally recommended for application every 3 to 5 years, long-term effects are also important. Generally, lime is considered satisfactory when 75% passes an 8- to 10-mesh screen. When a liming material passes an 8- to 10-mesh screen, it will also have finer particles that will pass finer-mesh sieves. Thus liming material generally has particles of various sizes.

Calcium oxide and calcium hydroxide are powdery materials and do not have problems with particle size.

## 6.12. BENEFITS OF LIMING

Liming improves soil pH and thus provides soil environments for better plant growth. It prevents toxicity due to excess Al and Mn, and the availability



**Figure 6.13.** The effect of limestone fineness on the response of crops to increased rates of limestone application. These are average data from a number of field experiments. (From Brady, N.C., 1990. *The Nature and Properties of Soils*, 11th ed. With permission of Prentice-Hall, Inc., Upper Saddle River, NJ.)

of P and Mo improves. Microbiological processes such as nitrification and nitrogen fixation also improve. Because of increased microbial activity and plant growth, liming may also indirectly improve the physical conditions of the soil.

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